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Description

The present invention relates to polymer/polyols using modified polyols. These polymer/polyols are sometimes termed polymeric polyols or graft polyols. The present invention also relates to processes by which such modified polyols are prepared and to processes of using the polymer/polyols derived from the modified polyols.

The reaction between a polyfunctional isocyanate and a polyfunctional alcohol to produce polyurethane foams, elastomers, resins and the like is a well known chemical reaction which is commercially exploited on a large scale. Commercial polyurethane manufacture in general involves the reaction between a polyfunctional isocyanate and a polyfunctional alcohol such as a polyether polyol. Such polyether polyols are made from a polyfunctional low molecular weight alcohol onto which has been added a polyalkylene oxide chain. The polyalkylene oxide chain is typically prepared from ethylene oxide, propylene oxide or a mixture thereof in a random or block form.

In recent years, the use of polyether polyols of the type described above has been in some areas superseded by polyether polyols containing additional polymeric matter. These polyether polyols, known as polymer/polyols have been described in US 3,304,273, US 3,383,351, US Reissued patent 28,715 and US Reissued patent 29,118. In general, such polymer/polyols have been prepared by polymerising one or more olefinically unsaturated monomers dispersed in the polyether polyol in the presence of a free radical catalyst. The polymer/polyols produced by this process, which are thought to comprise a polymer or copolymer of the monomers at least partially grafted to the polyether polyol, have the important advantage of imparting to the final polyurethane improved load-bearing properties as compared with earlier polyether polyols.

The need to obtain polyurethanes with further improved load-bearing properties has meant that recently attempts have been made to improve polymer/polyols further. In particular developments of polymer/polyols has centred around increasing the polymer content whilst still maintaining the polymer/polyol in the form of a low viscosity fluid having a resistance to polymer sedimentation.

In order to produce stable low viscosity polymer polyols, it has been proposed to introduce during the polymerisation an extra component termed a non aqueous dispersant (NAD) stabiliser. The NAD stabiliser comprises a polyol or polyether polyol, containing deliberately added unsaturation, which copolymerises or grafts to the growing polymer chains thereby forming a steric hinderance which prevents the agglomeration of particles.

An example of such an NAD stabiliser is given in US 3,823,201 where there is disclosed an unsaturated polyether polyol obtained by the reaction of a polyether polyol with the anhydride of an unsaturated acid, for example maleic anhydride. In this case, the anhydride of the unsaturated acid reacts with a free hydroxyl group on the polyether polyol to produce a polyether polyol having from about 0.10 to 0.70 mole of unsaturation per mole of polyol.

Similar methods of introducing unsaturation into a polyether polyol thereby forming a NAD stabiliser are disclosed in US 4,198,488, GB 1,411,646 and EP 6605.

DE-A-1595162 and GB-A-941291 disclose silicon compounds which can be used as NAD stabiliser although such a use is not taught.

It has now been found that polymer/polyol dispersions having favourable viscosity and resistance to sedimentation at high solids content can be prepared by polymerising one or more monomers having olefinic unsaturation in a polyether polyol containing a specific NAD stabiliser.

According to the present invention there is provided a fluid polymer/polyol dispersion prepared by polymerising, in the presence of a free radical catalyst, one or more olefinic monomers in a liquid polyol under polymerisation conditions characterised in that the liquid polyol comprises:

- (a) a base polyol comprising a first polyether polyol having a number average molecular weight in excess of 400 and a hydroxyl number in the range 20 to 280 and
- (b) a modified polyol prepared by reacting the first polyether polyol or a second polyether polyol having a number average molecular weight in excess of 400 and a hydroxyl number in the range 20 to 280 with a silicon containing compound having the formula $R_mSi(X)_{4-m}$ where (a) m is either 0 or 1, (b) the R groups are independently saturated hydrocarbyl groups or hydrogen and (c) the X groups are independently -OH, -OR¹ where R¹ is a C₁ to C₁₀ hydrocarbyl group, or halogen.

It is a feature of the NAD stabilisers of the present invention that, by using a specific coupling agent having 3 or 4 functional groups which are reactable with hydroxyl groups, the need to have any additional unsaturation in the coupling agent is avoided. Additional unsaturation however can also be present if desired to improve further the characteristics of the final NAD stabiliser.

The mechanism by which the NAD stabilisers of the present invention act is not understood in any detail. However, without being held to a particular mechanism, it is thought that the coupling agent couples together polyol molecules to form an extended network. Such a network is able, during

the preparation of the polymer/polyol, to prevent aggregation of polymeric material into particles large enough to sediment or modify the viscosity of the final product.

The polyols used in the preparation of the NAD stabiliser can be for example polyalkylene polyether polyols, polyhydroxyl containing polyesters, polyhydroxy terminated polyurethane polymers, and polyhydric polythioethers. A preferred class of polyols are the polyalkylene polyether polyols, usually called polyether polyols, of which the following sub-classes are the most preferred.

- (a) alkylene oxide adducts of non-reducing sugars and their derivatives
- (b) alkylene oxide adducts of polyphenols
- (c) alkylene oxide adducts of polyhydroxyalkanes.

The polyether polyol used should have a number average molecular weight in excess of 400 and a hydroxyl number in the range 20 to 280. Terms such as number average molecular weight and hydroxyl number will be familiar to those skilled on the art.

Most preferably the polyether polyol is a poly(ethylene oxide and/or propylene oxide) adduct of one of the following polyhydric alcohols; glycerol, trimethylolpropane, diethylene glycol, the isomeric butanetriols, pentanetriols and hexanetriols, and pentaerythritol.

As regards the coupling agent this can, in principle, be any of the specified silicon containing molecule having 3 or 4 functional groups which are able to react with the hydroxyl groups on the polyol providing that this coupling agent itself is not further degradable or decomposable by the polyol or under the conditions of the coupling reaction.

The silicon containing compounds are those having the generic formula $R_mSi(X)_{4-m}$ where (a) m is either 0 or 1, (b) the R groups are independently saturated hydrocarbyl groups or hydrogen and (c) the X groups are independently -OH, -OR', where R' is a C_1 to C_{10} hydrocarbyl group, or halogen. Preferably the R groups are substituted or unsubstituted C_1 to C_{10} alkyl groups. Examples of silicon compounds which are preferred include tetraethoxysilane, tetramethoxysilane, tetrachlorosilane, trichlorosilane.

Typically the NAD stabiliser is prepared by reacting the coupling agent with the polyol in an inert solvent, for example toluene, at a temperature in the range 60 to 160°C, preferably 100 to 120°C. The reaction is preferably carried out in the presence of a transesterification or transesterification catalyst for example, trifluoroacetic acid/sodium acetate mixtures or an amidine or guanidine catalyst. When an acid catalyst is used it may be necessary to add a neutralisation agent, for example sodium bicarbonate, at the end of the

reaction.

The reaction between the coupling agent and the polyol may be carried out as described above, however, where the reaction involves a halide compound or an alkyl or aryl sulphonate it may be necessary to form an alkali metal salt of the polyol prior to reaction with the coupling agent by, for example, treating the polyol with an alkali metal.

The NAD stabiliser produced by reactions of the type described above have preferably a viscosity in the range 500-4000 mPas at 25°C. In addition the NAD stabiliser should have less than 0.8% by weight preferably 0.3 to 0.7% by weight induced unsaturation.

As mentioned earlier, the NAD stabilisers described above are particularly useful for preparing polymer/polyol dispersions containing high levels of polymer. The fluid polymer/polyol dispersions are prepared by polymerising one or more monomers in a liquid polyol under polymerisation conditions and in the presence of a free radical catalyst characterised in that the liquid polyol comprises (1) a base polyol and (2) an NAD stabiliser of the type described above.

The base polyol used in the preparation of the polymer/polyol may be any of the polyols described above. The base polyols should have viscosities in the range 100-5000 mPas at ambient temperature, preferably in the range 100-2000 mPas.

During the preparation of the polymer/polyol dispersion, polymer is produced in the liquid base polyol by polymerisation of the olefinic monomer or monomers. The monomers used are suitably vinyl monomers for example styrene, acrylonitrile, methacrylonitrile and methyl methacrylate. Preferably a mixture of styrene and acrylonitrile are used to produce a copolymer. The final polymer/polyol dispersion is suitably one having more than 20% by weight polymer present and is preferably one having between 30 and 70% by weight polymer. As regards the relative amounts of styrene and acrylonitrile in the copolymer it is desirable for reasons of cost to be able to maximise the level of styrene present. Preferably the copolymer should contain 50 to 100% styrene on a molar basis.

The polymerisation reaction occurring during the preparation of the polymer/polyol dispersion is initiated by means of a free radical initiator. The free radical initiator can be any of those which are routinely used in vinyl polymerisation reactions including peroxides, perborates, persulphates, percarbonates and azo compounds. Typical examples of such free radical initiators include alkyl and aryl hydroperoxides, dialkyl and diaryl peroxides, dialkylperoxydicarbonates and azobis(nitriles). Preferred free radical initiators are azobis(isobutyronitrile) and bis(4-tertbutyl cyclohexyl) per-

oxydicarbonate (Perkadox).

The polymer/polyol dispersion produced using the NAD stabilisers of the present invention are useful in the preparation of polyurethanes, particularly polyurethane foams. Such polyurethane foams have improved tensile strength and load bearing without impairment of the other physical parameters associated with the product. Accordingly there is also provided a process for the production of a polyurethane foam by reacting a polyfunctional isocyanate with a fluid polymer/polyol dispersion of the type described above in the presence of

- (a) a catalyst for the urethane forming reaction,
- (b) a blowing agent and
- (c) a foam stabiliser

Polyfunctional isocyanates which can be used to advantage include diisocyanatoalkanes, e.g. 1,2-diisocyanatoethane, 1,3-diisocyanatopropane, the isomeric benzene, xylene and toluene diisocyanates and MDI.

Catalysts which can be used to accelerate the urethane forming reaction will likewise be familiar to those skilled in the art. These include amines, phosphines, strong inorganic bases, titanate, silicate and stannate esters and organo tin derivatives.

As regards blowing agents and foam stabilisers the range of materials which can be used will be familiar to the skilled man. Thus suitable blowing agents include water and halogenated hydrocarbons of low molecular weight.

The process may be carried out batchwise or continuously.

The invention is now illustrated by the following examples.

Preparation of NAD Stabiliser

Example 1 - Triethoxymethylsilane as coupling agent

A two litre reactor fitted with a mechanical stirrer, a thermometer and a Dean Stark apparatus lapped by a condensor was charged with a blend of trifluoroacetic acid (1.38g 12mmoles), potassium acetate (0.69g, 6.9 mmoles), toluene (400 ml), a polyether polyol (970g glycerol started, PO:86%, EO 14%, MW:3500, OH number 46.0 mg KOH/g, BP Product Polyurax U10-01-Polyurax is a Registered Trade Mark) and triethoxymethylsilane (16.5g, 92 mmoles).

The reaction mixture was then heated to 110°C for 2 hours. During this time the transesterification reaction between the polyether polyol and the triethoxymethylsilane took place producing the NAD stabiliser and ethanol. At 110°C a toluene/ethanol azeotrope started to boil and was removed by distillation through the Dean Stark apparatus. By monitoring the levels of ethanol in the

distillate using gas chromatography, it was found the reaction was practically complete in two hours.

Example 2 - Tetraethoxy silane as coupling agent.

A four litre reactor vessel equipped as described in Example 1 was charged with a blend of polyether (2000 g, glycerol started, PO:86%, EO:14%, MW:3500, OH Number:46.0 mg KOH/g, BP Product: Polyurax U10-01), trifluoroacetic acid (2.8 g, 24 mmoles) potassium acetate (1.40 g, 14 mmoles) and tetraethoxysilane (26.5 g, 126 mmoles).

The reaction was carried out as described in Example 1 for 3 h, then the mixture was neutralized with sodium bicarbonate (20.0 g, 238 mmoles). Solvent was then removed and the product filtered. It has a viscosity of 24000 mPas at 25°C, an OH number of 33.2 mg KOH/g, an acid number of 0.0009 mg KOH/g and an average MW of 17300.

Example 3 - Tetrachlorosilane as coupling agent

A four litre vessel equipped as described in Example 1 was charged with a blend of polyether (2000 g, glycerol started, PO:86%, EO:14%, MW:3500, OH Number:46.0 mg KOH/g, BP Product: Polyurax U10-01) and toluene (800 ml). Residual water in the polyol was removed by azeotropic distillation. To this blend, was added tetrachlorosilane (14 g, 93.6 mmoles).

The mixture was then heated with stirring at 60°C for 5 h. Solvent and hydrogen chloride released were then removed by vacuum distillation and the product was used as such without further acid trace neutralization. It had a viscosity of 6200 mPas at 25°C, an acid number of 0.0013 mg KOH/g, an OH number of 36.0 mg KOH/g and an average MW of 11300.

Examples 4 - Trichlorosilane as coupling agent.

An autoclave equipped with a thermometer, stirrer, heat exchange means was charged with a polyether (300 g, glycerol started, PO:86%, EO:14%, MW:3500, OH Number: 46.0 mg KOH/g, BP Product: Polyurax U10-01), toluene (150 ml) and trichlorosilane (3.80 g, 85 mmoles).

The mixture was stirred at 65°C for 5 h. Solvent and hydrogen chloride were then removed by vacuum distillation and the product was used as such without further neutralization. It had an OH number of 40.0 mg KOH/g.

Preparation of Copolymer Dispersion

Comparative Experiment A: Use of Polyol without added stabilizer

In a one litre reactor equipped as described above, was charged a base polyether (210 g of the above example) without any added stabilizer. With stirring and under a slight nitrogen flow, the charge was heated to 125°C, and a stream of styrene (90.65 g, 21%), acrylonitrile (38.85 g, 9%) and a polymerization initiator (Perkadox P-16, 2.65 g, 0.5%-Perkadox is a Registered Trade Mark) dispersed in the above described polyether (90.0 g) was continuously added to the charge during two hours period. Before completion of the addition, a completely coagulated mass of polymer was obtained, blocking the stirrer.

Example 5

In a one litre reactor equipped with a thermometer, stirrer, dropping funnel and heat exchanger, was charged with a blend of a base polyether (210g, glycerol started, PO:86%, EO:14%) and the stabilizer of Example 2 (26.5 g, 5%). With stirring and under a slight nitrogen flow, the charge was heated to 125°C, and a stream of styrene (141.2 g, 26.6%), acrylonitrile (60.5 g, 12%) and a polymerization initiator (Perkadox P-16, 2.65 g, 0.5%) dispersed in the above described base polyether (90.0 g) was continuously added to the charge during two hours period. Upon completion of addition, the reaction mixture was maintained at 125°C for 1 hour. The reaction mixture was then stripped of volatiles for two hours at 110°C, under less than 13,3 mbar (10 mm of mercury). The stripped reaction product, a white opaque stable dispersion, had a viscosity of 5500 mPas at 25°C.

Example 6 - All polystyrene polymer dispersion

In a one litre reactor equipped as described in Example 5, was charged with a blend of a base polyether (of Example 5, 210 g), and the stabilizer of Example 2 (28.30 g, 5%). With stirring and under a slight nitrogen flow, the charge was heated to 125°C, and a stream of styrene (232 g, 41%), and a polymerization initiator (azobisisobutyronitrile, AIBN, 5.66 g, 1%) dispersed in the above base polyether (90 g) was continuously added to the charge during two hours period. Upon completion of addition, the reaction mixture was maintained at 125°C for 1 hour. The reaction mixture was then stripped of volatiles for two hours at 110°C, under less than 13,3 mbar (10 mm of mercury). The stripped reaction product, a white opaque stable dispersion, (38% polymer), has a viscosity of 2000 mPas at 25°C.

Example 7 - All polystyrene polymer dispersion

In a one litre reactor equipped as described in

Example 5, was charged with a blend of a base polyether (of Example 5, 210 g), and the stabilizer of Example 2 (28.30 g, 5%). With stirring and under a slight nitrogen flow, the charge was heated to 125°C, and a stream of styrene (232 g, 41%), and a polymerization initiator (azobisisobutyronitrile, AIBN, 5.66 g, 1%) dispersed in the above base polyether (90 g) was continuously added to the charge during two hours period. Upon completion of addition, the reaction mixture was maintained at 125°C for 1 hour. The reaction mixture was then stripped of volatiles for two hours at 110°C, under less than 13,3 mbar (10 mm of mercury). The stripped reaction product, a white opaque stable dispersion, (37% polymer), had a viscosity of 2500 mPas at 25°C.

In the above examples the abbreviation h, stands for hours.

The above examples show that the modified polyether polyols are suitable for preparing stable acrylonitrilestyrene polymer/polyol dispersions in excess of 30% w/w polymer content without a highly viscous product being formed.

Claims

1. A fluid polymer/polyol dispersion prepared by polymerising, in the presence of a free radical catalyst, one or more olefinic monomers in a liquid polyol under polymerisation conditions characterised in that the liquid polyol comprises:
 - (a) a base polyol comprising a first polyether polyol having a number average molecular weight in excess of 400 and a hydroxyl number in the range 20 to 280 and
 - (b) a modified polyol prepared by reacting the first polyether polyol or a second polyether polyol having a number average molecular weight in excess of 400 and a hydroxyl number in the range 20 to 280 with a silicon containing compound having the formula $R_mSi(X)_{4-m}$ where (a) m is either 0 or 1, (b) the R groups are independently saturated hydrocarbyl groups or hydrogen and (c) the X groups are independently -OH, -OR¹ where R¹ is a C₁ to C₁₀ hydrocarbyl group, or halogen.
2. A fluid polymer/polyol dispersion as claimed in claim 1 characterised in that the silicon containing compound used to make the modified polyol is selected from the group consisting of tetraethoxysilane, tetramethoxysilane, tetrachlorosilane and trichlorosilane.
3. A fluid polymer/polyol dispersion as claimed in either claim 1 or claim 2 characterised in that

the fluid polymer/polyol dispersion contains more than 20% by weight polymer.

4. A fluid polymer/polyol dispersion as claimed in claim 3 characterised in that the fluid polymer/polyol dispersion contains between 30 and 70% by weight polymer.
5. A fluid polymer/polyol dispersion as claimed in claim 4 characterised in that the polymer dispersed in the liquid polyol contains 50 to 100% styrene on a molar basis.
6. A fluid polymer/polyol dispersion as claimed in claim 1 characterised in that the modified polyol has a viscosity in the range 500-4000 mPas at 25°C.
7. A fluid polymer/polyol dispersion as claimed in any one of claims 1 to 6 characterised in that polymer is a copolymer of styrene and acrylonitrile.
8. A process for preparing polyurethane foam characterised in that the process comprises reacting a polyfunctional isocyanate with a fluid polymer/polyol dispersion of a type defined in any one of claims 1 to 7 in the presence of a catalyst for the urethane forming reaction, a blowing agent and a foam stabiliser.

Revendications

1. Dispersion fluide polymère/polyol, préparée par polymérisation, en présence d'un catalyseur générateur de radicaux libres, d'un ou plusieurs monomère(s) oléfinique(s) dans un polyol liquide, dans des conditions de polymérisation, caractérisée en ce que le polyol liquide comprend:
 - (a) un polyol de base, comportant un premier polyol polyéther ayant une masse molaire moyenne en nombre de plus de 400 et un indice d'hydroxyle situé dans l'intervalle allant de 20 à 280,
 - (b) un polyol modifié préparé par réaction du premier polyol polyéther ou d'un deuxième polyol polyéther, ayant une masse molaire moyenne en nombre de plus de 400 et un indice d'hydroxyle situé dans l'intervalle allant de 20 à 260, avec un dérivé du silicium ayant la formule $R_mSi(X)_{4-m}$, où (a) m est 0 ou 1, (b) les groupes R sont, indépendamment, des groupes hydrocarbonés saturés ou l'atome d'hydrogène et (c) les groupes X sont, indépendamment, -OH, -OR¹, où R¹ est un groupe hydrocarboné en C₁ à C₁₀, ou un atome d'halogène.

2. Dispersion fluide polymère/polyol telle que revendiquée dans la revendication 1, caractérisée en ce que le dérivé du silicium utilisé pour produire le polyol modifié est choisi dans le groupe constitué par le tétraéthoxysilane, le tétraméthoxysilane, le tétrachlorosilane et le trichlorosilane.
3. Dispersion fluide polymère/polyol telle que revendiquée dans la revendication 1 ou la revendication 2, caractérisée en ce que la dispersion fluide polymère/polyol contient plus de 20% en poids de polymère.
4. Dispersion fluide polymère/polyol telle que revendiquée dans la revendication 3, caractérisée en ce que la dispersion fluide polymère/polyol contient entre 30% et 70% en poids de polymère.
5. Dispersion fluide polymère/polyol telle que revendiquée dans la revendication 4, caractérisée en ce que le polymère dispersé dans le polyol liquide contient un pourcentage molaire 50 à 100% de styrène.
6. Dispersion fluide polymère/polyol telle que revendiquée dans la revendication 1, caractérisée en ce que le polyol modifié a une viscosité dans la zone de 500 à 4000 mPa.s à 25°C.
7. Dispersion fluide polymère/polyol telle que revendiquée dans l'une quelconque des revendications 1 à 6, caractérisée en ce que le polymère est un copolymère de styrène et d'acrylonitrile.
8. Procédé pour préparer une mousse de polyuréthane, caractérisé en ce que le procédé comprend la mise en réaction d'un isocyanate polyfonctionnel avec une dispersion fluide polymère/polyol d'un type défini dans l'une quelconque des revendications 1 à 7, en présence d'un catalyseur pour la réaction de formation de l'uréthane, d'un agent de gonflement et d'un agent stabilisant de la mousse.

Patentansprüche

1. Flüssige Polymer/Polyol-Dispersion hergestellt durch Polymerisieren, in Anwesenheit eines freien-Radikal-Katalysators, eines oder mehrerer olefinischer Monomere in einem flüssigen Polyol unter Polymerisationsbedingungen, dadurch gekennzeichnet, daß das flüssige Polyol umfaßt:
 - (a) ein Ausgangspolyol umfassend ein erstes Polyetherpolyol mit einem

- Molekulargewicht-Zahlenmittel über 400 und einer Hydroxylzahl im Bereich von 20 bis 280 und
- (b) ein modifiziertes Polyol hergestellt durch Umsetzen des ersten Polyetherpolyols oder eines zweiten Polyetherpolyols mit einem Molekulargewicht-Zahlenmittel über 400 und einer Hydroxylzahl im Bereich von 20 bis 280 mit einer Silicium enthaltenden Verbindung mit der Formel $R_mSi(X)_{4-m}$, wobei (a) m entweder 0 oder 1 ist, die R-Gruppen unabhängig gesättigte Kohlenwasserstoffgruppen oder Wasserstoff sind und (c) die X-Gruppen unabhängig -OH, OR¹ sind, wobei R¹ eine C₁ bis C₁₀ Kohlenwasserstoffgruppe oder Halogen ist.
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2. Flüssige Polymer-/Polyol-Dispersion wie in Anspruch 1 beansprucht, dadurch gekennzeichnet, daß die Silicium enthaltende Verbindung, die zur Herstellung des modifizierten Polyols verwendet wird, ausgewählt ist aus der Gruppe bestehend aus Tetraethoxysilan, Tetramethoxysilan, Tetrachlorsilan und Trichlorsilan.
- 20
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3. Flüssige Polymer-/Polyol-Dispersion wie in entweder Anspruch 1 oder Anspruch 2 beansprucht, dadurch gekennzeichnet, daß die flüssige Polymer-/Polyol-Dispersion mehr als 20 Gewichts-% Polymer enthält.
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4. Flüssige Polymer-/Polyol-Dispersion wie in Anspruch 3 beansprucht, dadurch gekennzeichnet, daß die flüssige Polymer-/Polyol-Dispersion zwischen 30 und 70 Gewichts-% Polymer enthält.
- 35
5. Flüssige Polymer-/Polyol-Dispersion wie in Anspruch 4 beansprucht, dadurch gekennzeichnet, daß das in flüssigem Polyol dispergierte Polymer 50 bis 100 % Styrol auf molarer Basis enthält.
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6. Flüssige Polymer-/Polyol-Dispersion wie in Anspruch 1 beansprucht, dadurch gekennzeichnet, daß das modifizierte Polyol eine Viskosität im Bereich von 500 - 4000 mPas bei 25 °C hat.
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7. Flüssige Polymer-/Polyol-Dispersion wie in einem der Ansprüche 1 bis 6 beansprucht, dadurch gekennzeichnet, daß das Polymer ein Copolymer von Styrol und Acrylnitril ist.
- 50
8. Verfahren zur Herstellung von Polyurethanschaum, dadurch gekennzeichnet, daß das Verfahren das Umsetzen eines polyfunktionalen Isocyanats mit einer flüssigen Polymer-
- 55
- /Polyol-Dispersion einer Art, die in einem der Ansprüche 1 bis 7 definiert ist, in Anwesenheit eines Katalysator für die Urethanbildungsreaktion, eines Treibmittels und Schaumstabilisators umfaßt.

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(54) **Polymer-modified polyols
useful in polyurethane manufacture**

(57) A polymer-modified polyol is formed by polymerising an olamine, particularly an alkanolamine, with an organic polyisocyanate in the presence of a polyol. The alkanolamine reacts polyfunctionally

with the polyisocyanate to produce polyaddition products.

The polyaddition products may constitute a stable dispersion in the polyol and the resulting polymer-modified polyol is particularly useful as a polyol starting material for reaction with a polyisocyanate in the manufacture of polyurethane foam.

GB 2 072 204 A

SPECIFICATION

Polymer-modified polyols useful in polyurethane manufacture

This invention relates to polymer-modified polyols useful in polyurethane manufacture.

Polyurethane foam is manufactured by reacting a polyol with a polyisocyanate in the presence of a blowing agent and usually also one or more other additives.

In order to modify the physical properties of the resulting foam in a desired manner, it is known to use pre-formed polymer-modified polyols (i.e. polyols containing additional polymeric material) in the polyurethane-forming reaction. Thus, for example, British Patent 1,501,172 describes the use of polyol dispersions of polyaddition products of polyisocyanate and primary amines, secondary amines, hydrazines or hydrazides; and British Patent 1,482,213 describes the use of polyols having dispersed therein and also copolymerised therewith polymeric material derived from the *in situ* polymerisation of ethylenically unsaturated monomers.

An object of the present invention is to provide further polymer-modified polyols which may be useful in polyurethane manufacture.

According to the invention therefore there is provided a method of forming a polymer-modified polyol wherein an olamine is polymerised with an organic polyisocyanate in the presence of a polyol, the olamine reacting at least predominantly polyfunctionally with the isocyanate.

With the method of the invention, the olamine (by which is meant an organic compound having one or more hydroxyl (—OH) groups and also one or more amine groups whether primary, secondary or tertiary (—NH_2 , =NH , =N) acts as a polyfunctional reactant (having two or more reactive hydrogens) and a polyaddition product is formed with the polyisocyanate (by which is meant a compound having two or more isocyanate groups). Where the olamine is a primary or secondary amine, it has alcohol and amine groups with active hydrogens all of which hydrogens may be reactive with regard to the isocyanate. Where the olamine is a tertiary amine it has multiple alcohol groups with active hydrogens all of which may be reactive with regard to the isocyanate. In each case all or only some of the reactive hydrogens may in fact react. It is believed that the polyaddition reaction produces straight and/or branched chains by combination of isocyanate and hydroxyl groups to form urethane linkages (—NH—CO—O—) and by combination of isocyanate and amine groups to form urea linkages (—NH—CO—NH— or =N—CO—NH—) as appropriate. The said polyaddition product may be mixed and/or chemically combined (as by copolymerisation) with the polyol and it is to be understood that the term polymer-modified polyol as used herein is intended to encompass both physical and chemical combinations and also mixtures thereof, although it is believed that, most usually, the

method of the invention will result in a predominantly physical combination. Such physical combination may be in the form of a solution or a stable dispersion of the polyaddition product in the polyol depending on the starting materials used. In particular, the choice of the olamine and possibly also the polyol may determine the physical state of the polymer-modified polyol.

Most preferably, with the method of the invention, the olamine and the isocyanate are mixed in the molar ratio of about 1.0/0.5 to 1.0/1.5 in the presence of a polyether polyol having a molecular weight in the range 200 to 10,000 (particularly 2800—7000) and the reacted olamine and polyisocyanate together constitute 1% to 35% by weight based on the weight of the polyol.

Any suitable alkanolamine or combination of alkanolamines may be used as the olamine of the present invention including but not restricted to primary, secondary and tertiary alkanolamines such as Monoethanolamine, diethanolamine, triethanolamine, N-Methylethanolamine, N-Ethylethanolamine, N-Butylethanolamine, N-Methyldiethanolamine, N-Ethyldiethanolamine, N-Butyldiethanolamine, Monoisopropanolamine, Diisopropanolamine, Triisopropanolamine, N-Methylisopropanolamine, N-Ethylisopropanolamine, N-Propylisopropanolamine. The term alkanolamine as used herein includes substituted alkanolamines and, for example, it is also possible to use primary and secondary alkanolamines which are halogen substituted at the nitrogen atom, or secondary or tertiary alkanolamines which are halogen substituted at the alkyl group (i.e. the alcohol group replaced by a halogen atom). In a particularly preferred embodiment, triethanolamine is used as the alkanolamine.

Whilst it is visualised that the method of the present invention will most usually utilise an alkanolamine, particularly an open chain aliphatic alkanolamine, as the olamine it is to be understood that it may also be possible to use other olamine compounds which have hydroxyl and amine groups attached to carbo-cyclic, aromatic or heterocyclic nuclei or combinations thereof with each other and/or with open chain aliphatic nuclei.

Any suitable organic polyisocyanate may be used including aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic polyisocyanates such as are known for use in the polyisocyanate/polyol polyurethane forming reaction (see for example British Patent No. 1,453,258).

Suitable commercially readily available polyisocyanates include 2, 4 and 2, 6 tolylene diisocyanates also mixtures of these isomers (called in general TDI), polyphenyl polymethylene polyisocyanates of the type obtained by condensing aniline with formaldehyde, followed by phosgenation (called in general crude MDI), and polyisocyanates containing carbodiimide groups, urethane groups, allophanate groups, isocyanate groups, urea

groups or biuret groups (called in general polyisocyanates).

Any suitable polyol may be used including polyether polyols having a molecular weight in the range of 200 to 10,000 such as are known for use in the polyisocyanate/polyol polyurethane forming reaction and as described for example in British Patent No. 1,482,213. Such known polyether polyols can be obtained by reaction of alkylene oxides with active hydrogen containing compounds, the molecular weight of the reaction product depending on the amount of alkylene oxide reacted.

The polyaddition products obtained according to the present invention may be modified by the proportionate use of monofunctional isocyanates, amines or N-dialkylalkanolamines. For example, the average molecular weight of the polyaddition products may be adjusted by incorporating monofunctional compounds of this type in proportions of up to 25 mole percent based upon the olamine component.

Suitable monofunctional isocyanates include methyl, ethyl, isopropyl, isobutyl, hexyl, lauryl, and stearyl isocyanate, cyclohexyl isocyanate, phenyl isocyanate, tolylisocyanate 4-chlorophenyl isocyanate and diisopropyl phenyl isocyanate.

Suitable monofunctional amines include dialkylamines such as dimethylamine, diethylamine, dibutylamine, cyclohexylamine, and suitable N-dialkylalkanolamines include dimethylethanolamine and diethylethanolamine.

It is to be understood that not all alcohol/amine groups of the olamine used in the polyaddition reaction of the invention need react in all circumstances with the isocyanate and thus the olamine may react monofunctionally in some instances thereby to act in itself as a chain terminator.

If desired, the polyaddition reaction of the present invention can be catalysed by introduction of substances such as those conventionally used as catalysts in the polyisocyanate/polyol polyurethane forming reaction. Thus organometallics such as stannous octoate and dibutyl tin dilaurate and/or amines such as triethylenediamine can be used. The amount of catalyst used may be small in relation to that normally used in the polyurethane forming reaction, for example of the order of 0.02% rather than 0.2% of the total weight of polyol, although larger amounts may also be used if desired.

The reaction using a primary or secondary alkanolamine may not require catalysis but this may be advantageous with a tertiary alkanolamine such as triethanolamine.

The molecular weight of the polyaddition product may be adjusted by varying the quantitative ratio between the olamine on the one hand and the polyisocyanate on the other hand (and by monofunctional components if they are used). Thus, for example, although a molar ratio of olamine to polyisocyanate of 1.0/0.5 to 1.0/1.5 is preferred and substantially equivalent molar quantities are particularly preferred, it is possible

to use a higher proportion of isocyanate if appropriate allowance can be made for the higher viscosity or even rapid gellation which tends to occur at higher isocyanate levels. An upper ratio of say 1.0/1.55 or 1.0/1.6 may thus be possible. As the quantity of isocyanate is reduced the molecular weight of the polyaddition product also decreases together with the viscosity. In general an olamine/organic polyisocyanate molar ratio of 1.0/0.8 to 1.0/1.1 is preferred.

It is even possible substantially to exceed the above mentioned upper ratio limit of 1 to 1.6 if a "capping" agent is introduced to limit cross-linking and hence gellation. Thus, although it may normally be preferable to utilise reaction conditions which result in bifunctional reaction of the olamine with the isocyanate, in some circumstances and with some olamines, particularly triethanolamine, it may be preferable to obtain trifunctional reaction of the olamine with the isocyanate thereby to ensure that there are substantially no free hydroxyl groups which could undesirably interfere with a subsequent polyurethane-forming reaction using the polymer-modified polyol. In this latter case an olamine/isocyanate ratio of up to say 1.0/2.1 or higher may be desirable and a capping agent (say N-dimethylethanolamine) may be added (say in an olamine/capping agent ratio of 1.0/1.2) to limit cross-linking.

Although the concentration of the reacted olamine and isocyanate (and hence the polyaddition products) in the polyether polyol may vary within wide limits it should generally be between 1 and 35% by weight, preferably from 3 to 30% by weight. Where a specific concentration of polyaddition product is required (for example for use in the manufacture of polyurethane foams having certain optimal properties a concentration of about 10% by weight may be required) this may be obtained directly by appropriate selection of the reactants to give the required concentration or alternatively by subsequent dilution of a formed polyaddition product with additional polyether polyol as appropriate.

In general the reactants may be mixed at temperatures from 0°C, or above their melting points, whichever may be lower, up to 150°C. Preferably the reactants are mixed at room temperature or just above their melting points, whichever may be lower, up to 70°C. It may also be possible to mix the reactants below their melting points.

The reaction is exothermic and a temperature rise is observed according to the proportion of polyaddition product made, based upon the weight of the polyether polyol.

The more efficient the mixing of the reactants the finer the particle size of the dispersion (where a dispersion is produced) and the lower the viscosity. Although a simple batch process may be used, whereby one of the olamine and polyisocyanate reactants is first of all dissolved or dispersed in the polyether polyol, followed by addition of the other into the zone of maximum

agitation, in-line blending of the materials may also be used. In the latter case all reactants are pumped at controlled rates and may be mixed simultaneously or one reactant may be mixed firstly with the polyether polyol followed by addition and mixing of the other reactant.

The dispersion of polyether polyol may be used either immediately after completion of the reaction or after a prolonged period of time. For example, the polyaddition product in a polyether polyol may be metered from an in-line blending unit, where the reaction takes place, directly into the mixing head of a polyurethane production machine, of a well-known type. Where the reaction of the diamine with the polyisocyanate is relatively slow, then an intermediate holding tank may be used between such in-line blending unit and the polyurethane mixing head to allow additional time for complete reaction to take place.

Additives such as activators, stabilizers, crosslinkers, water, blowing agents, flame-proofing agents and pigment pastes, may be added to the polymer-modified polyol of the present invention either during or after reaction.

The polyaddition product of the present invention can be used in the manufacture of polyurethane foam. In the case where the product is in the form of a stable polyol dispersion, that is a dispersion which does not settle out or at least will remain in dispersion during mixing with other foam-forming ingredients, the dispersed polyaddition product is particularly effective as a polymeric filler in the production of highly resilient conveniently processible foam, such dispersed product acting to build strength whilst at the same time rupturing cell walls.

In the case where the product is in the form of a polyol solution, this may be suitable for the use in forming polymeric material having properties different from those obtained with polyol dispersions.

In general, where the polyaddition product is in the form of a stable dispersion, this is suitable for processing into soft, semi-hard and hard polyurethane foams having improved properties, such as increased hardness, and non-shrinking foams of the high resilience type which are well-known in the industry, can be prepared since the polyol dispersed polyaddition product has a cell opening effect. In addition the dispersions are also suitable for the production of for example elastomers, coverings and coatings based on polyurethanes.

Where the dispersion is to be used in making a polyurethane, usually the polyurethane forming process will utilise the polyol of the dispersion and thus the properties of the polyol of the dispersion, particularly its hydroxyl number and functionality, will be selected in known manner in dependence upon the type of polyurethane being made. For example for the preparation of elastomers the polyether polyol will preferably be predominantly linear, i.e. difunctional and will have hydroxyl numbers in the range 30 to 170. For the

preparation of foams, the polyether polyols are selected in known manner to give foams which are flexible, semi-flexible or rigid. Thus for the preparation of flexible foams the polyether polyols preferably have hydroxyl numbers in the range 20 to 80 and from 2 to 4 hydroxyl groups per molecule for example ICI Polyol PBA 1233. If desired mixtures of polyether polyols can be used.

Organic polyisocyanates which may be used in making the polyurethanes have been described in the prior art and may be the same as the organic polyisocyanates described above for reaction with the diamine.

The polyurethane foaming reaction mixture may also contain other conventional ingredients of such reaction mixture according to the type of polyurethane being made. Thus, the reaction mixture may contain catalyst, for example tertiary amines and organic tin compounds, cross-linking or chain lengthening agents, for example diethanolamine, triethanolamine, ethylene glycol, glycerol, dipropylene glycol and phenylene diamine, flame-proofing agents, for example halogenated alkyl phosphates and fillers for example barium sulphate.

For the preparation of foams, blowing agents are included in the reaction mixture. Examples of suitable blowing agents include water which reacts with the polyisocyanate forming carbon dioxide and inert volatile liquids which vaporise under the influence of the exothermic reaction or due to the release of pressure if a mechanical frothing process is used. Examples of such liquids are halogenated hydrocarbons having boiling points not exceeding 100°C at atmospheric pressure and preferably not exceeding 50°C, especially chlorofluorinated hydrocarbons such as trichlorofluoromethane and dichlorodifluoromethane also chlorinated hydrocarbons such as dichloromethane. The amount of blowing agent is selected in known manner to provide foams of the desired density. In general from 0.005 to 0.3 mole of gas per 100 grams of reaction mixture is suitable. If desired, the density of the foam produced can be modified by over-packing, that is to say foaming the reaction mixture in a closed mould having a volume less than that which would be occupied by the resultant foam if the reaction mixture were allowed to rise freely.

In general, the composition of the polyurethane-forming reaction mixture should be such that the ratio of isocyanate groups to active hydrogen atoms is substantially within the range 0.9/1 to 1.2/1 but higher ratios may be used if desired.

When a polyurethane foam is prepared it is usually necessary to stabilize or regulate the cells which are formed by the addition of a foam stabilizer or cell regulator such as polysiloxane—polyalkylene oxide block copolymers which may contain direct carbon to silicon or carbon to oxygen to silicon bonds between the organic and polysiloxane units. When producing 'high resilience' polyurethane foams then dimethyl

silicone oils or low molecular weight modifications thereof are satisfactory, for example Theodore Goldschmidt AG silicon B8616.

One shot, prepolymer or quasi prepolymer methods may be employed as may be appropriate for the particular type of polyurethane being made.

The components of the polyurethane forming reaction mixture may be mixed together in any convenient manner, for example by using any of the mixing equipment described in the prior art for the purpose. If desired, some of the individual components may be pre-blended so as to reduce the number of component streams requiring to be brought together in the final mixing step. It is often convenient to have a two-stream system whereby one stream comprises a polyisocyanate or prepolymer and the second stream comprises all the other components of the reaction mixture.

The invention is illustrated but not limited by the following Examples in which all parts are by weight and percentages by weight. Unless otherwise stated ambient temperatures were used for reactants.

The abbreviations used in the Examples for the polyethers have the following meanings.

Polyether A:

A glycerol-started polyether of propylene oxide tipped with 15% ethylene oxide to an hydroxyl number of 35 and a primary hydroxyl number of approximately 75%.

Polyether B:

A trimethylol propane-started polyether of propylene oxide tipped with ethylene oxide to an OH number of 34 and a primary OH group content of approximately 80%.

Polyether C:

A glycerol-started polyether of propylene oxide and ethylene oxide to an OH number of 47 and a primary OH group content of less than 5%.

Polyether D:

A linear polypropylene glycol with an OH number of 56 containing secondary hydroxyl groups.

EXAMPLE 1

900 gms. of polyether A at a temperature of 20°C was blended with 48.7 gms. of triethanolamine at a temperature of 20°C under conditions of high speed mixing 51.2 gms. of a mixture of 80% 2.4 and 20% 2.6 tolylene diisocyanate was added over a period of five seconds. 0.3 gms. of dibutyl-tin-dilaurate catalyst was then added and a fast reaction took place and the temperature of the mixture rose from 20°C to 37°C over a period of three minutes from the time of completion of addition of the catalyst.

On cooling the resulting stable dispersion with 10% solids had a viscosity of 1600 cps. at 25°C.

300 gms. of the above product was placed in a beaker followed by 7.8 gms. of water, 3 gms. of diethanolamine, 0.21 gms. of bis (2 dimethyl

aminoethyl) ether and 1.5 gms. of Goldschmidt Silicon B8616 and stirred, the temperature being adjusted to 22°C. Next was added 0.75 gms. of dibutyl-tin-dilaurate and stirred for 10 seconds followed by the addition of 117 gms. of a mixture of 80% of 2.4 and 20% of 2.6 tolylene diisocyanate. After a further five seconds the mixture was poured into a box and expansion started. After a further 105 seconds from the end of mixing a non-shrinking 'high resilience' foam had been produced with the following properties.

Density Kgs./m ³	34
CLD g/cm ² (1)	28
Resilience % (2)	63

(1) Resistance to a compression at 40% deflection.
(2) Ball rebound %.

EXAMPLE 2

920 gms. of polyether A at 20°C were added to a beaker and 32.1 gms. of diethanolamine at 30°C was added at room temperature with mechanical stirring. 47.9 gms. of a mixture of 80% of 2.4 and 20% of 2.6 tolylene diisocyanate were added over a period of 30 seconds into the vortex of the stirred mixture. A white stable dispersion was formed and the temperature had risen from 20°C to 37°C within 30 seconds of completion of the addition of the isocyanate. The polyaddition product contained the isocyanate and alkanolamine in the molar ratio of 0.9 to 1.0 and the final product contained 8.0% of the polyaddition product in polyether polyol and had an acceptable viscosity at ambient temperature.

300 gms. of the above product was placed in a beaker followed by 7.8 gms. of water, 3 gms. of diethanolamine, 0.21 gms. of bis (2 dimethyl aminoethyl) ether and 1.5 gms. of Goldschmidt Silicone B8616 and stirred, the temperature being adjusted to 22°C. Next was added 0.75 gms. of dibutyl-tin-dilaurate and stirred for 10 seconds followed by the addition of 117 gms. of a mixture of 80% of 2.4 and 20% of 2.6 tolylene diisocyanate. After a further five seconds the mixture was poured into a box and expansion started. After a further 105 seconds from the end of mixing a non-shrinking 'high resilience' foam had been produced with properties similar to Example 1.

EXAMPLE 3

A foam was prepared according to the method as described in Example 2 except that 300 gms. of the polyaddition product in polyether polyol was replaced by 300 gms. of the polyether polyol (polyether A) and only 100 gms. of the isocyanate was used. Expansion to produce a foam took place as in Example 2 except that the resulting foam shrank, the properties being unmeasurable.

EXAMPLE 4

The polyaddition product in polyether polyol was prepared using polyether A according to Example 2 and was foamed also according to Example 2 except that all of the dibutyl-tin-dilaurate was replaced by 0.6 gms. of stannous octoate. A non-shrinking foam was obtained of the high resilience type with properties similar to those of Example 1.

EXAMPLE 5

A polyaddition product was prepared and foamed according to Example 2 except that the polyether A was replaced with polyether B. The stable dispersion in polyether polyol had a solids content of 8% and an acceptable viscosity of ambient temperature. The resulting foam was non-shrinking and had properties similar to those of Example 1.

EXAMPLE 6

A polyaddition product in polyether A was prepared according to Example 2 except that the molar ratio of isocyanate to alkanolamine was 1.1 to 1.0, the total solids content remaining at 8%. The resulting product had a high but usable viscosity in excess of 2500 cps. at 25°C. Foaming according to Example 2 gave a high resilience non-shrinking foam.

EXAMPLE 7

A polyaddition product in polyether A was prepared according to Example 2 except that the molar ratio of isocyanate to alkanolamine was 0.45 to 1.0 and the total solids content was 8%. Foaming according to Example 2 gave a shrinking foam. The properties of this foam could not be measured.

EXAMPLE 8

A polyaddition product was produced by taking 920 gms. of polyether A at a temperature of 20°C and mixing with 24.5 gms. diethanolamine at a temperature of 30°C followed by 55.5 gms. of crude MDI with vigorous agitation. A polyaddition product in a polyether polyol was obtained having a solids content of 8% and a usable but high viscosity in excess of 3000 cps. at 25°C.

The product was foamed according to Example 2 giving a non-shrinking foam of the high resilience type.

EXAMPLE 9

A stable dispersion in polyether C at a temperature of 20°C was prepared by taking 800 gms. of polyether C and adding 80.24 gms. of diethanolamine at a temperature of 30°C which was stirred at high speed prior to and during the addition of 119.75 gms. of a mixture of 80% 2,4 and 20% 2,6 tolylene diisocyanate which took place over a period of one minute. A temperature rise of 29°C was observed and the product on cooling had an acceptable viscosity at ambient temperature and a solids content of 20%.

EXAMPLE 10

A stable dispersion was prepared according to Example 9 except that polyether C was replaced by polyether D. The resulting polyaddition compound in polyether D had a solids content of 20% and an acceptable viscosity at ambient temperature.

The stable dispersion produced in accordance with the foregoing Examples 1, 2, 5—10 are of a non-ionic nature. That is, the dispersions contain covalent polymeric substances which are devoid of ionic groups. Moreover, substantially no water or other ionic medium is used in the preparation of (nor is present in) the dispersions. In this latter respect the presence of traces of water, such as will tend to be contained in commercially available polyols and other starting materials, may be acceptable although in general the presence of water is undesirable and should be kept at as low a level as possible. Preferably the water content should not be greater than 1% by weight and most preferably the content is very much less than this, say below 0.1%, although it is to be understood that in some circumstances it may be possible to operate the process of the invention at water levels above 1%.

The polyols used in performing the process of the invention may be of the triol kind containing predominantly primary hydroxyl groups in so far as such polyols are of particular use as starting materials for the formation of polyurethane foams. However, since the production of polymer-modified polyols in accordance with the process of the invention, and particularly the production dispersions as described in the above Examples, involves reaction of the isocyanate wholly or predominantly with the amine with the polyol acting wholly or predominantly as an unreacted carrier, it will be appreciated that it is possible to use any suitable polyol selected in particular in accordance with the requirements of a subsequent polyurethane-forming reaction in which the polymer-modified polyol is to be used. Thus for example polyols which are triols and/or diols and which have primary and/or secondary hydroxyl groups or any other suitable structures may be used.

CLAIMS

1. A method of forming a polymer-modified polyol wherein a starting material is polymerised with an organic polyisocyanate in the presence of a polyol, characterised in that the starting material is an amine and this reacts at least predominantly polyfunctionally with the isocyanate.

2. A method according to claim 1, characterised in that the amine is an alkanolamine.

3. A method according to claim 2, characterised in that the alkanolamine and the isocyanate are mixed in the molar ratio of about 1.0/0.5 to 1.0/1.5 in the presence of a polyether polyol having a molecular weight in the range 200 to 10,000 and the reacted alkanolamine and

polyisocyanate together constitute 1% to 35% by weight based on the weight of the polyol.

4. A method according to claim 3, characterised in that the alkanolamine and the isocyanate are reacted in the molar ratio of 1/0.8 to 1/1.1.

5. A method according to claim 2, characterised in that the alkanolamine and the isocyanate are reacted in a molar ratio in excess of 1/1.6 in the presence of a chain capping agent.

6. A method according to claim 3 or 4, characterised in that the alkanolamine and the polyisocyanate together constitute 3% to 30% by weight based on the weight of the polyol.

7. A method according to any one of claims 3, 4 or 6, characterised in that the total weight of the alkanolamine and the polyisocyanate is greater than 10% based on the weight of the polyol and after polymerisation of the alkanolamine with the isocyanate further polyol is added to dilute the polymer-modified polyol.

8. A method according to any one of claims 2 to 7, characterised in that the alkanolamine is triethanolamine.

9. A method according to any one of claims 2 to 8, characterised in that the polyisocyanate is an aromatic diisocyanate.

10. A method according to any one of claims 2 to 9, characterised in that a catalyst is mixed with the alkanolamine and the polyisocyanate to catalyse the said polymerisation reaction therebetween.

11. A method according to claim 10, characterised in that said catalyst is selected from organometallics and amines.

12. A method according to any one of claims 2 to 11, characterised in that additives are mixed with the alkanolamine and the polyisocyanate to modify the said polymerisation reaction

therebetween.

13. A method according to claim 12, characterised in that said reaction-modifying additives are selected from monofunctional isocyanates, monofunctional amines and dialkylalkanolamines.

14. A method of forming a polymer-modified polyol according to claim 1, substantially as hereinbefore described in Examples 1, 2, 4, 5, 6, 8, 9 or 10.

15. A polymer-modified polyol when made by the method of any one of claims 1 to 14.

16. A polymer-modified polyol comprising a polyol and a polyaddition product resulting from the reaction of an olamine at least predominantly polyfunctionally with an organic polyisocyanate.

17. A polymer-modified polyol according to claim 15 or 16, which is a stable dispersion.

18. A method of forming a polyurethane wherein an isocyanate is reacted with a polyol characterised in that said polyol comprises a pre-formed polymer-modified polyol as claimed in any one of claims 15 to 17.

19. A method according to claim 18, characterised in that the isocyanate which reacts with the polyol is the same as that used in forming the polymer-modified polyol.

20. A method according to claim 18 or 19, characterised in that said polyurethane-forming reaction between the isocyanate and the polyol is carried out in the presence of additives selected from blowing agents, catalysts, stabilizers, cross-linking agents, flame-proofing agents, pigments, fillers.

21. A method according to claim 18, substantially as hereinbefore described in the accompanying Examples.

22. A polyurethane formed by the method of any one of claims 18 to 21.